

~~PCT/EP98/07148~~

a

## a

The invention relates to unsaturated fatty  
5 alcohols which are obtained by fractionating palm oil  
fatty acid methyl esters, and then hydrogenating the  
fraction of unsaturated long-chain methyl esters, and  
to a process for the preparation of these fatty  
alcohols.

10

### Statement of Related Art

Unsaturated fatty alcohols are important intermediates for a large number of products of the chemical industry, such as, for example, for the preparation of surfactants and skincare products. A review on this topic can be found, for example, by U. Ploog et al. in *Seifen-Öle-Fette-Wachse [Soaps-Oils-Fats-Waxes]* 109, 225 (1983). They are prepared from more or less unsaturated fatty acid methyl esters which can be hydrogenated, for example, in the presence of chromium- or zinc-containing mixed catalysts [Ullmann's *Encyclopedia of Industrial Chemistry*, Verlag Chemie, Weinheim, 4th Edition, Vol. 11, p. 436 ff]. The prior art is a large-scale process, as has hitherto also been carried out by the applicant, according to which animal fats and oils are used, and the unsaturated fatty alcohols produced after the hydrogenation are distilled at a still temperature of e.g. 220 to 250°C and a reduced pressure of from 1 to 20 mbar - measured at the top of the column. Since the preparation of unsaturated fatty alcohols is associated with high costs, distillation has been carried out with as low a raw material loss as possible. In fact, in this way, it was possible to achieve a yield of about 90% of theory, and correspondingly a loss of 10%, although the products exhibited a marked intrinsic odor. A further disadvantage is that the fatty alcohols of the prior art have unsatisfactory storage and low-temperature behavior.

For application reasons, unsaturated fatty alcohols having iodine numbers of from 50 to 80 are particularly preferred since these have a solidification point which is favorable for use in cosmetic products. Unsaturated fatty alcohols having iodine numbers in the abovementioned range are currently largely based on animal raw materials. The desired iodine number range is set by blending different products having differing iodine number ranges. Adjustment of the iodine number range by distillative methods is not possible since the iodine number or iodine number range of animal-based fatty acids or fatty alcohols remains virtually constant during fractionation. However, animal fats have the disadvantage that they have a very heterogeneous structure. For example, animal fats contain nitrogen-containing compounds, such as amides or steroids, such as, for example, cholesterol, which are directly or indirectly responsible for the abovementioned unpleasant odor of the products. The nitrogen-containing compounds can become involved in secondary reactions, which impairs product stability, in particular oxidation stability, and leads to discolored products. In addition, because of the continuing BSE debate, products which are prepared using beef tallow are viewed extremely critically by the consumer. In the cosmetics market, there is therefore a continuous need for ever purer raw materials of ever higher quality, a demand which can usually only be met by ever more complex industrial processes and additional purification steps. In the case of unsaturated fatty alcohols, there is, in particular, the need for products having improved color and odor quality and a more advantageous low-temperature behavior. Added to this is the fact that in recent years consumer behavior has changed to the effect that consumers place very great value on purely vegetable products. The known vegetable fatty alcohols have iodine numbers in the range below 20 or very high iodine numbers above 100.

Fatty alcohols having iodine numbers in the abovementioned range between 20 and 95, which is particularly preferred with regard to application technology, are not known. The blending of fatty alcohols having very different iodine numbers does not lead to satisfactory products. German Laid-open Specification DE-A1 4335781 (Henkel) discloses a process in which the triglycerides present in the vegetable fats or raw materials are firstly cleaved by pressurized cleavage into glycerol and fatty acids, and the latter are esterified with methanol, or the starting materials are directly transesterified to give the fatty acid methyl esters and then the esters are hydrogenated to give the alcohols, either the fatty acid methyl esters or the hydrogenation products being fractionated by removal of an amount of forerunnings such that the end product has an iodine number of from 20 to 110 and a conjugene content of less than 4.5% by weight. Whilst the process can be used for vegetable raw materials such as palm oil for the preparation of unsaturated fatty alcohols in the iodine number range 50 to 65 without problems, if palm oil is used to produce unsaturated fatty alcohols in the iodine number range from 65 to 85, results are obtained which are surprisingly not entirely satisfactory.

The object of the present invention was consequently to provide unsaturated fatty alcohols based on palm oil which have iodine numbers in the range from 65 to 85 and, compared with animal-based unsaturated fatty alcohols, have greater oxidation stability and comparable or better low-temperature behavior. The aim was also to obtain extremely pure coupled products.

#### Description of the invention

The invention provides unsaturated palm oil fatty alcohols having an iodine number in the range from 65 to 85, which essentially comprise unsaturated fatty alcohols and mixtures of saturated fatty alcohols of the formula (I)

R<sup>1</sup>OH

(I)

in which R<sup>1</sup> is a saturated or unsaturated, linear or  
5 branched alkyl radical having 14 to 20 carbon atoms,  
obtainable by

- (a) fractionating palm oil fatty acid methyl esters  
into a predominantly saturated C<sub>16</sub> distillate and a  
predominantly unsaturated C<sub>16/18</sub> bottom product, and
- 10 (b) hydrogenating the bottom product with retention of  
the double bonds to give the corresponding  
alcohols.

Surprisingly, we have found that, by the  
process according to the invention, it is now possible  
15 for the first time to obtain unsaturated fatty  
alcohols, even those based on palm oil, in the iodine  
number range from 65 to 85 and which have good color  
and oxidation stability and excellent low-temperature  
behavior; additionally, the products are virtually  
20 odorless. A further advantage is that a very pure  
palmitic acid methyl ester fraction is obtained as an  
intermediate, which can be further processed  
separately.

The invention further provides a process for  
25 the preparation of unsaturated palm oil fatty alcohols  
having an iodine number in the range from 65 to 85,  
which essentially comprise unsaturated fatty alcohols  
and mixtures of saturated fatty alcohols of formula (I)

30 R<sup>1</sup>OH

(I)

in which R<sup>1</sup> is a saturated or unsaturated, linear or  
branched alkyl radical having 14 to 20 carbon atoms, in  
which

- 35 (a) palm oil fatty acid methyl esters are fractionated  
into a predominantly saturated C<sub>16</sub> distillate and a  
predominantly unsaturated C<sub>16/18</sub> bottom product, and

- (b) the bottom product is hydrogenated with retention of the double bonds to give the corresponding alcohols.

#### Fractionation

5           The fractionation of the palm oil fatty acid methyl esters can be carried out batchwise or continuously at reduced pressure. Heating can, for example, be by means of superheated steam, a still temperature of e.g. 220 to 250°C normally prevailing.

10   The actual fractionation takes place in a packed column containing low-pressure-loss internals. Suitable internals are, for example, arranged sheet-metal packings. Other examples can be found in **RÖMPP Chemie Lexikon, Thieme Verlag, Stuttgart, 9th Edition, Vol. 3,**

15   **p. 2305 (1990)** under the heading "Kolonnen-Einbauten" [Column internals] and in the literature cited therein. The required fine vacuum of 1 to 20 mbar at the top of the column can be achieved, for example, using water-ring pumps and upstream steam jets. The pressure drop

20   over the entire distillation unit should preferably be no more than 20 mbar. A distillate containing predominantly saturated C<sub>16</sub> portions and a bottom product containing predominantly unsaturated C<sub>16</sub>-C<sub>18</sub> portions are obtained in the process. The weight ratio

25   of distillate to bottom product is in the range from 30:70 to 35:65.

#### Hydrogenation

          The subsequent hydrogenation of the predominantly unsaturated methyl ester fraction

30   obtained as bottom product with retention of the double bonds can be carried out in a manner known per se, i.e. for example in the presence of commercially available zinc/chromium catalysts, at temperatures in the range from 250 to 350°C and a hydrogen pressure of from 200

35   to 275 bar. The conjugene content of the products is in the range from 6 to 12% by weight, and the content of hydrocarbons is below 3% by weight, preferably below 1% by weight.

### Industrial applicability

The unsaturated palm oil fatty alcohols obtained by the process according to the invention are low in color and odor and have a particularly advantageous low-temperature behavior. They are therefore suitable as raw materials for the preparation of washing, rinsing and cleaning products, and also products for hair care and body care, in which they can be present in amounts of from 1 to 50% by weight, preferably 5 to 30% by weight, based on the compositions.

	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041	2042	2043	2044	2045	2046	2047	2048	2049	2050	2051	2052	2053	2054	2055	2056	2057	2058	2059	2060	2061	2062	2063	2064	2065	2066	2067	2068	2069	2070	2071	2072	2073	2074	2075	2076	2077	2078	2079	2080	2081	2082	2083	2084	2085	2086	2087	2088	2089	2090	2091	2092	2093	2094	2095	2096	2097	2098	2099	2100	2101	2102	2103	2104	2105	2106	2107	2108	2109	2110	2111	2112	2113	2114	2115	2116	2117	2118	2119	2120	2121	2122	2123	2124	2125	2126	2127	2128	2129	2130	2131	2132	2133	2134	2135	2136	2137	2138	2139	2140	2141	2142	2143	2144	2145	2146	2147	2148	2149	2150	2151	2152	2153	2154	2155	2156	2157	2158	2159	2160	2161	2162	2163	2164	2165	2166	2167	2168	2169	2170	2171	2172	2173	2174	2175	2176	2177	2178	2179	2180	2181	2182	2183	2184	2185	2186	2187	2188	2189	2190	2191	2192	2193	2194	2195	2196	2197	2198	2199	2200	2201	2202	2203	2204	2205	2206	2207	2208	2209	2210	2211	2212	2213	2214	2215	2216	2217	2218	2219	2220	2221	2222	2223	2224	2225	2226	2227	2228	2229	2230	2231	2232	2233	2234	2235	2236	2237	2238	2239	2240	2241	2242	2243	2244	2245	2246	2247	2248	2249	2250	2251	2252	2253	2254	2255	2256	2257	2258	2259	2260	2261	2262	2263	2264	2265	2266	2267	2268	2269	2270	2271	2272	2273	2274	2275	2276	2277	2278	2279	2280	2281	2282	2283	2284	2285	2286	2287	2288	2289	2290	2291	2292	2293	2294	2295	2296	2297	2298	2299	2300	2301	2302	2303	2304	2305	2306	2307	2308	2309	2310	2311	2312	2313	2314	2315	2316	2317	2318	2319	2320	2321	2322	2323	2324	2325	2326	2327	2328	2329	2330	2331	2332	2333	2334	2335	2336	2337	2338	2339	2340	2341	2342	2343	2344	2345	2346	2347	2348	2349	2350	2351	2352	2353	2354	2355	2356	2357	2358	2359	2360	2361	2362	2363	2364	2365	2366	2367	2368	2369	2370	2371	2372	2373	2374	2375	2376	2377	2378	2379	2380	2381	2382	2383	2384	2385	2386	2387	2388	2389	2390	2391	2392	2393	2394	2395	2396	2397	2398	2399	2400	2401	2402	2403	2404	2405	2406	2407	2408	2409	2410	2411	2412	2413	2414	2415	2416	2417	2418	2419	2420	2421	2422	2
--	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	---

Example

A technical-grade palm oil fatty acid methyl ester was fractionated in a packed column containing low-pressure-loss internals at a still temperature of 200°C and a head vacuum of 20 mbar, 30% by weight of palmitic acid methyl ester being produced as distillate, while in the still 70% by weight of a C<sub>16/18</sub> fatty acid methyl ester mixture remained, which had an iodine number of 74. The ester mixture from the still was transferred to an autoclave and reduced therein in the presence of commercially available zinc/chromium catalysts at 300°C and 250 bar with hydrogen to give the mixture of the corresponding alcohols. The hydrogenation product freed from methanol had, according to gas-chromatographic and wet-chemical analysis, the following characteristics:

Table 1:

Characteristics for the hydrogenation product

Composition	Portion [area %]	Specification	Value
Cetyl alcohol	18.3	Iodine number	74
Palmoleyl alcohol	0.5	Hydroxyl number	212
Margarinyl alcohol	0.6	Acid number	0.02
Stearyl alcohol	8.5	Saponification number	0.4
Oleyl alcohol	61.2	Hazen color number	10
Linolyl alcohol	3.3	Conjuene content	6.6% by wt.
Linolenyl alcohol	6.7	Solidification point	22.7°C
Hydrocarbons	0.9		